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# Stereoisomerism in Pentaerythritol-Bridged Cyclotriphosphazene Tetra-Spiranes: Spiro and Ansa 1,3-Propanedioxy Di-substituted Derivatives

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## Abstract

Four isomeric products were isolated and purified from the reaction of 1,3-propanediol with the tetra-spirane cyclophosphazene-organophosphate compound (**1**): viz. the di-monospiro (**2a**), di-monoansa (**2b**) and two monospiro-monoansa derivatives (**2c**) and (**2d**). It is shown by <sup>31</sup>P NMR spectroscopy on addition of a chiral solvating agent (CSA) that both the di-monospiro (**2a**) and di-monoansa (**2b**) derivatives are racemates, as expected, whereas no splitting of NMR signals occurred on addition of CSA to solutions of (**2c**) and (**2d**). It is found by X-ray crystallography that the two monospiro-monoansa spirane derivatives, (**2c**) and (**2d**), are meso diastereoisomers, which represent a new case of the stereochemistry of bis di-substituted cyclophosphazene derivatives of (**1**). It is also observed from the <sup>31</sup>P NMR spectrum of the reaction mixture, supported by the yields of pure compounds, that formation of a spiro group is about 4.5 times more likely than that of an ansa moiety under the conditions of the reaction.

## Keywords:

Cyclotriphosphazene derivatives, NMR spectroscopy, Tetrspiranes, X-ray diffraction

## Introduction

Difunctional reagents with cyclophosphazenes can give rise to four structural types; spiro, ansa, bridged and open chain.<sup>[1]</sup> For example, the reaction of 1,3-propanediol with cyclotriphosphazene,  $\text{N}_3\text{P}_3\text{Cl}_6$ , gave spiro,  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_3\text{O}]_x\text{Cl}_{6-x}$  ( $x = 1,2,3$ ); ansa,  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_3\text{O}]\text{Cl}_4$ ; spiro-ansa,  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_3\text{O}]_2\text{Cl}_2$ ; open chain,  $\text{N}_3\text{P}_3[\text{O}(\text{CH}_2)_3\text{OH}]\text{Cl}_5$  and bridged,  $\text{N}_3\text{P}_3\text{Cl}_5[\text{O}(\text{CH}_2)_3\text{O}]\text{N}_3\text{P}_3\text{Cl}_5$  compounds, in which spiro derivatives are by far the major product.<sup>[2]</sup> It is known that reaction of cyclotriphosphazene with a tetrafunctional alcohol such as pentaerythritol,  $\text{C}(\text{CH}_2\text{OH})_4$ , gives a spirane-bridged compound (**1**), whose structure (Figure 1) consists of four six-membered rings, each joined by a tetrahedral atom (phosphorus or carbon atom) to the next ring, with each six-membered ring being orthogonal to its neighbours.<sup>[3]</sup> The stereochemistry of bis di-substituted cyclophosphazene derivatives of (**1**) has recently been elucidated;<sup>[4]</sup> it was shown that racemates were observed for bis geminal derivatives, as well as for non-geminally di-substituted *cis* and *trans* (the latter has two diastereoisomers) derivatives. In the present work, the reaction of the spirane-bridged compound (**1**) with 1,3-propanediol was investigated and four isomeric di-substituted spiro and ansa derivatives (**2a–d**) were isolated (Figure 1). Two of the products (**2a–b**) gave rise to chiral compounds corresponding to cases observed previously (bis di-substitution that is geminal or *cis* non-geminal),<sup>[4]</sup> whereas the other two derivatives (**2c–d**) have geminal di-substitution in one cyclophosphazene ring and *cis* non-geminal disubstitution in the other cyclophosphazene ring, giving rise to a new case of chirality in such systems, in which both compounds are meso diastereoisomers.

## Results and Discussion

The spirane-bridged compound, (**1**), was allowed to react with 1,3-propanediol in a 1:2 mole ratio to give four di-substituted isomers (**2a–d**) which were separated by column chromatography. Overall there was a yield of about 25% with compound (**2a**, 14.9%) being the major product, and with minor yields of (**2b**, 2.5%) (**2c**, 4%) and (**2d**, 3.5%). Characterization of the products was initially done by elemental analysis, mass spectrometry and  $^{31}\text{P}$  NMR spectroscopy. Elemental analysis and mass spectrometry give the same results for the four compounds, as expected for isomers. The proton-decoupled  $^{31}\text{P}$  NMR spectra of (**2a**) and (**2b**) are observed (Figure 2a and 2b, respectively) as ABX spin systems resulting

from the two phosphazene rings in each compound having the same substitution pattern. However, the two ABX spin systems are quite different as in (**2a**) the X-part is *ca.* 26-27 ppm and the AB portion is 8-11 ppm, whereas the X-part of (**2b**) is *ca.* 11 ppm and the AB portion is 30-32 ppm. The assignment of signals of (**2a**) was assisted by proton-coupled  $^{31}\text{P}$  NMR spectra [not shown] which indicates that the 26-27 ppm signal corresponds to a  $>\text{PCl}_2$  group (no coupling) and the AB portion results from the  $>\text{P}(\text{bridge})$  and  $>\text{P}(\text{spiro})$  groups. The  $^{31}\text{P}$  NMR spectrum of (**2b**) at 30-32 ppm is characteristic of a cyclotriphosphazene dioxy-ansa derivative with a relatively small ansa ring<sup>[5]</sup> and the signal at 11 ppm is given by the  $>\text{P}(\text{bridge})$  group; the ansa moiety is observed as an AB spin system because (**2b**) is a chiral diastereoisomer (see below). The  $^{31}\text{P}$  NMR spectra are consistent with (**2a**) being the di-monospiro compound and (**2b**) being the di-monoansa compound. The  $^{31}\text{P}$  NMR spectra of (**2c**) and (**2d**) (Figure 2c and 2d, respectively) are very similar to each other and consist of five multiplets resulting from the superposition of an  $\text{A}_2\text{X}$  and an ABX spin system; the ABX spin system is similar to that for the spiro derivative, (**2a**), and the  $\text{A}_2\text{X}$  has similar chemical shifts and coupling constants to those found for the ansa derivative, (**2b**), but is  $\text{A}_2$  rather than AB because compound (**2b**) is a meso diastereoisomer (see below).  $^{31}\text{P}$  NMR indicates that both (**2c**) and (**2d**) are monospiro-monoansa compounds, having slightly different chemical shifts and coupling constants, especially for the spiro-substituted ring. The  $^{31}\text{P}$  NMR data for compounds (**2a**)–(**2d**) are summarised Table 1.

By analogy with previous work on the stereochemistry of bis di-substituted cyclophosphazene derivatives of (**1**),<sup>[4]</sup> it is expected that both compounds (**2a**) and (**2b**) are chiral and exist as racemates. The di-monospiro compound (**2a**) is the case of a bis geminal derivative and the di-monoansa compound (**2b**) has non-geminal di-substituents that are *cis*.<sup>[4]</sup> On addition of a chiral solvating agent [CSA, (*S*)-(+)-2,2,2-trifluoro-1-(9'-anthryl)ethanol] it was found that all the  $^{31}\text{P}$  NMR signals of compounds (**2a**) and (**2b**) exhibit chemical shift changes indicating complexation with the CSA, and that all signals, except the  $>\text{P}(\text{bridge})$  group of compound (**2b**), separate into two lines of equal intensity consistent with compounds (**2a**) and (**2b**) existing as racemates. The change in  $^{31}\text{P}$  NMR chemical shifts and separation of signals of compounds (**2a**) and (**2b**) at a 20:1 mole ratio of CSA:(**2a** or **2b**) are summarised Table 1. Addition of CSA to compounds (**2c**) and (**2d**) also caused changes in chemical shifts of each signal (Table 1), but no separation of signals even at higher mole ratios of 50:1 (**2c**) and 40:1 (**2d**). These results indicate that CSA complexes to compounds (**2c**) and (**2d**) in solution, and that both molecules may be meso, because CSA does not cause extra splitting of the NMR peaks. Such a caveat needs to be made, in the first instance,

because previous NMR work has shown splitting of peaks for meso compounds with remote stereogenic centres on addition of CSA (and Chiral Shift Reagents, CSR).<sup>[6]</sup> However, in the case of compounds (**2c**) and (**2d**) the centres of chirality in the cyclophosphazene ansa moiety are part of the same ring and only two bonds apart and so complexation with CSA will affect both centres at the same time, as is normally found for other analogous systems,<sup>[6]</sup> *i.e.* the anomalous <sup>31</sup>P NMR effect with CSA is not expected for compounds (**2c**) and (**2d**) and so both are expected to be meso compounds.

Although NMR spectroscopy has been used to show that both compounds (**2c**) and (**2d**) are different monospiro-monoansa derivatives, such data cannot be used to assign an absolute structure and hence compounds (**2c**) and (**2d**) were characterised by X-ray crystallography. The crystal structures of (**2c**) and (**2d**) (Figure 3) show that both molecules contain six rings, two phosphazene units bridged by a pentaerythritol molecule in a spirane arrangement, a spiro-O(CH<sub>2</sub>)<sub>3</sub>O unit in one cyclophosphazene ring and an ansa-O(CH<sub>2</sub>)<sub>3</sub>O moiety in the *cis*-configuration in the other cyclophosphazene ring.<sup>[7]</sup> In both (**2c**) and (**2d**) the cyclophosphazene ring is essentially planar for the spiro-containing moiety, whereas for the ansa-substituted moiety the cyclophosphazene ring is non-planar, indicating strain which is relieved by the ring nitrogen atom containing the ansa moiety being significantly out of plane; 0.262 Å (**2c**) and 0.289 Å (**2d**).<sup>[8]</sup> The difference between the two structures is that in (**2c**) the ansa- and spiro-propanedioxy units are in a syn arrangement, whereas in (**2d**) there is an anti arrangement of the ansa- and spiro-propanedioxy units. The syn and anti structures are shown diagrammatically in Figure 1 for (**2c**) and (**2d**), respectively, from which it can be clearly seen that both molecules have a plane of symmetry and so are not chiral, as indicated by <sup>31</sup>P NMR spectroscopy. The stereochemistry of bis di-substituted cyclophosphazene derivatives of (**1**) has recently been elucidated<sup>[4]</sup> and compounds (**2c**) and (**2d**) give rise to a new case of stereochemistry of these spirane derivatives.

The <sup>31</sup>P NMR spectrum of the reaction mixture of compound (**2**) is shown in Figure 2(e). Using the NMR data in Table 1, it is possible to assign all the <sup>31</sup>P NMR signals in the reaction mixture to the four di-substituted compounds (**2a**)–(**2d**) (*i.e.* there is no evidence of the starting material, mono-substituted or higher substituted compounds). Assuming similar relaxation times for <sup>31</sup>P NMR signals of phosphorus nuclei with similar substitution patterns, the analysis gives spiro-spiro (**2a**, *ca.* 70%), syn spiro-ansa (**2c**) = anti spiro-ansa (**2d**) = *ca.* 12% and ansa-ansa (**2b**, *ca.* 6%), which corresponds to the formation of a spiro being about 4.5 times more likely than that of an ansa moiety. This was confirmed by the similar relative distribution of compounds observed as a result of isolation and purification after column

chromatography (**2a**, *ca.* 60%; **2b** *ca.* 10%; **2c** *ca.* 16%; **2d** *ca.* 14%), though the results do not match exactly, because there are likely to be small differences in the efficiency of isolation and purification of the four compounds. The preference for spiro over ansa 1,3-propanedioxy derivatives of cyclophosphazene is not surprising given that the spiro ring is a six-membered thermodynamically-stable chair form, in contrast to the eight-membered strained ansa ring.<sup>[8]</sup> In fact, it is somewhat surprising that significant quantities of the ansa derivatives are formed. However, in the reactions of cyclophosphazenes with diols in THF solution it has been observed<sup>[9–12]</sup> that the formation of ansa-derivatives is promoted by using the more reactive sodium alkoxides (rather than the less reactive neutral pentaerythritol and tertiary base used previously<sup>[3]</sup>). It was also expected<sup>[11,12]</sup> that addition of 15-crown-5 ether (which should make the nucleophilic alkoxide more reactive by reducing ion-pairing) might also assist in the formation of ansa derivatives with 1,3-propanediol in this work. The reaction conditions for the formation of spiro and ansa derivatives of cyclophosphazenes with diols are currently being investigated.

## Experimental Section

### Materials

Hexachlorocyclotriphosphazene (Shin Nisso Kako Co Ltd) was purified by fractional crystallisation from hexane. The following chemicals were obtained from Merck: pentaerythritol (>98%), 1,3-propanediol (>98%), silica gel 60, tetrahydrofuran ( $\geq 99.0\%$ ), dichloromethane ( $\geq 99.0\%$ ), ethyl acetate ( $\geq 99.0\%$ ), *n*-hexane (>96%), sodium hydride (>60%), 15-crown-5 ether (>98%). The deuteriated solvent (CDCl<sub>3</sub>) for NMR spectroscopy was obtained from Apollo Scientific and the chiral solvating agent (CSA), (*S*)-(+)-2,2,2-trifluoro-1-(9'-anthryl)ethanol, from Aldrich Chem. Co.

### Methods

Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using the fast atom bombardment (FAB) method (35 kV) with MNBA as the matrix; <sup>35</sup>Cl values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed on Merck Silica gel plates (Merck, Kieselgel 60, 0.25mm thickness) with F<sub>254</sub> indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230-400 mesh; for 3g. crude mixture, 100g.

silica gel was used in a column of 3 cm in diameter and 60 cm in length).  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions on a Bruker DRX 500 MHz spectrometer using 85%  $\text{H}_3\text{PO}_4$  as an external reference for  $^{31}\text{P}$ . In order to assign the signals of some compounds both proton-coupled and proton-decoupled  $^{31}\text{P}$  NMR spectra were recorded. Experiments involving the chiral solvating agent (CSA) were performed by addition of small aliquots of a concentrated solution of CSA in the solvent used for NMR spectroscopy and the proton-decoupled  $^{31}\text{P}$  NMR spectrum recorded at each addition.

### X-Ray crystallography

X-ray structure determination and crystallographic data were collected by means of combined phi and omega scans on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode ( $\lambda\text{Mo-k}_\alpha = 0.71073\text{\AA}$ ). The structures were solved by direct methods, SHELXS-97 and refined using SHELXL-97.<sup>[13]</sup> Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV.<sup>[14]</sup> The structure of **2c** exhibits crystallographic disorder about the mirror axis in the space group. In addition a disordered solvent molecule was also present, but was too disordered to resolve and was therefore removed from the model using the SQUEEZE<sup>[15]</sup> procedure from within the PLATON<sup>[16]</sup> suite of programs.

### Synthesis

**The reaction of compound (1) with 1,3-propanediol to give compounds (2a–d).** Compound (1) was prepared as in the literature.<sup>[3]</sup> To a stirred solution of compound (1) (2 g, 2.92 mmol) dissolved in 20 mL of dry tetrahydrofuran at  $-15^\circ\text{C}$  under an argon atmosphere was first added dropwise 1,3-propanediol (0.4 g, 5.84 mmol) in 20 mL of dry tetrahydrofuran, then sodium hydride (0.28 g, 11.68 mmol) in 20 mL of dry tetrahydrofuran was added dropwise and finally 15-crown-5 (0.5 g) was added. The reaction mixture was stirred for a further 2 days at room temperature and the reaction was followed by TLC indicating four products and no starting material remaining. The precipitated salt (NaCl) was then filtered off, the solvent was removed under reduced pressure and four products were isolated by column chromatography [silicagel 60 (70-230 mesh) as adsorbent and ethyl acetate/*n*-hexane



(1:2) as eluent]. The order of compounds eluted is **(2d)**, **(2b)**, **(2a)** and **(2c)**. Compound **(2c)** was crystallized from benzene and **(2d)** was crystallized from dichloromethane-hexane (3:1). **(2a)** 0.30 g, 14.85 %, mp 208°C), (found: C, 18.96; H, 2.85; N, 12.05 %;  $[M+1]^+$ , 690.8; **(2b)** 0.05 g, 2.47 %, decomp.200°C), (found: C, 21.06; H, 2.86; N, 12.11 %;  $[M+1]^+$ , 691.0 **(2c)** 0.08 g, 3.97 %, mp 170°C), (found: C, 20.25; H, 2.89; N, 12.12 %;  $[M+1]^+$ , 690.7. **(2d)** 0.07 g, 3.47 %, decomp.140°C), (found: C, 20.21; H, 2.74; N, 11.96 %;  $[M+1]^+$ , 690.7;  $C_{11}H_{20}Cl_4N_6O_8P_6$  requires C, 19.09; H, 2.91; N, 12.15 %;  $M^+$ , 690.0.

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- [7] The starting material, compound **(1)**, is a linear tetra-spirane, in which all the organophosphate and cyclotriphosphazene spirane moieties are six-membered and the shape of the ring system may be described as planar/chair/chair/planar. The introduction

of spiro substituents creates further six-membered spirane rings, whereas ansa substituents form eight-membered rings giving rise to fused bicyclic systems. Thus the spiro-spiro derivative, (**2a**), is a hexa-spirane with the two terminal spirane rings at an angle to the linear central four. The ansa-ansa compound, (**2b**), is a tetra-spirane with both ends having fused bicyclic units. The two spiro-ansa isomers, (**2c** and **2d**), are penta-spiranes and have one end with a fused bicyclic structure. The ring system of the syn compound (**2c**) may be described as chair/planar/chair/disordered-chair/fused-envelope and the anti compound (**2d**) as chair/planar/twisted-chair/chair/fused-envelope. All the CH<sub>2</sub> groups are staggered with respect to their nearest neighbours and eclipsed with those two bonds away, except in the twisted chair, where they are staggered.

- [8] The fused bicyclic ansa structures exhibit a boat-chair form. The ring N atom sandwiched between the two P-O ansa segments is forced out of the rest of the plane of the N<sub>2</sub>P<sub>3</sub> ring to such an extent that it is nearly parallel with the adjacent P-Cl bonds. This distortion causes a ring compression. The respective non-bonded P...P distances for the spiro and ansa N<sub>3</sub>P<sub>3</sub> rings for these two diastereoisomers are for the syn compound (**2c**) (spiro 2.724, 2.729 and 2.763 Å and ansa **2.636**, 2.725 and 2.726 Å) and for the anti compound (**2d**) (spiro 2.745, 2.760 and 2.764 Å and ansa **2.637**, 2.735 and 2.741 Å).
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<b>Table 1</b> $^{31}\text{P}$ NMR parameters of compounds ( <b>2a</b> )–( <b>2d</b> ) and the effect of addition of CSA <sup>a</sup>									
Compound		Ansa moiety			Spiro moiety			Coupling constants $^2J(\text{PP})/\text{Hz}$	
No	Struct.	Chemical shifts /ppm		$^2J(\text{PP})/\text{Hz}$	Chemical shifts /ppm				
		>P(ansa)	>P(bridge)		>P(Cl <sub>2</sub> )	>P(bridge)	>P(spiro)		
		1	2	3	1,3; 2,3	1	2	3	1,2 1,3 2,3
(i) $^{31}\text{P}$ NMR parameters of spirane compounds									
<b>2a</b>	sp-sp					26.55	10.43	8.69	71.7 68.8 87.1
<b>2b</b>	an-an	31.31; 31.08	11.05	74.3; 72.8 48.6 (1,2) <sup>b</sup>					
<b>2c</b>	sp-an syn	31.21; 31.21	11.09	73.5	26.42	10.48	8.77	71.0	68.5 87.9
<b>2d</b>	sp-an anti	31.20; 31.20	11.00	73.5	26.65	10.45	8.61	72.5	68.9 86.5
(ii) Effect of addition of CSA on chemical shifts (ppb) and $^2J(\text{PP})$ at 20:1 mole ratio									
<b>2a</b>	sp-sp $\Delta\delta^c$				43 [35]	-75 [8]	-13 [15]	71.6	68.5 86.8
<b>2b</b>	an-an $\Delta\delta^c$	10; [4];	22 [7]	-76 [d]	73.8; 72.5 48.6 (1,2) <sup>b</sup>				
<b>2c</b>	sp-an syn <sup>d</sup>	12		-108	73.2	53	-77	-22	70.9 68.3 87.6
<b>2d</b>	sp-an anti <sup>e</sup>	16		-82	73.4	24	-60	-5	72.3 68.6 86.2

<sup>a</sup> 202.45 MHz  $^{31}\text{P}$  NMR measurements in  $\text{CDCl}_3$  solutions at 298K. CSA is chiral solvating agent, (S)-(+)-2,2,2-trifluoro-1-(9'-anthryl)ethanol.

<sup>b</sup> AB coupling for  $^2J(\text{PP})/\text{Hz}$  is ansa ring

<sup>c</sup>  $\Delta\delta$  is the difference in chemical shift (ppb) of racemic signals at a mole ratio of CSA:(**2**) of 20:1

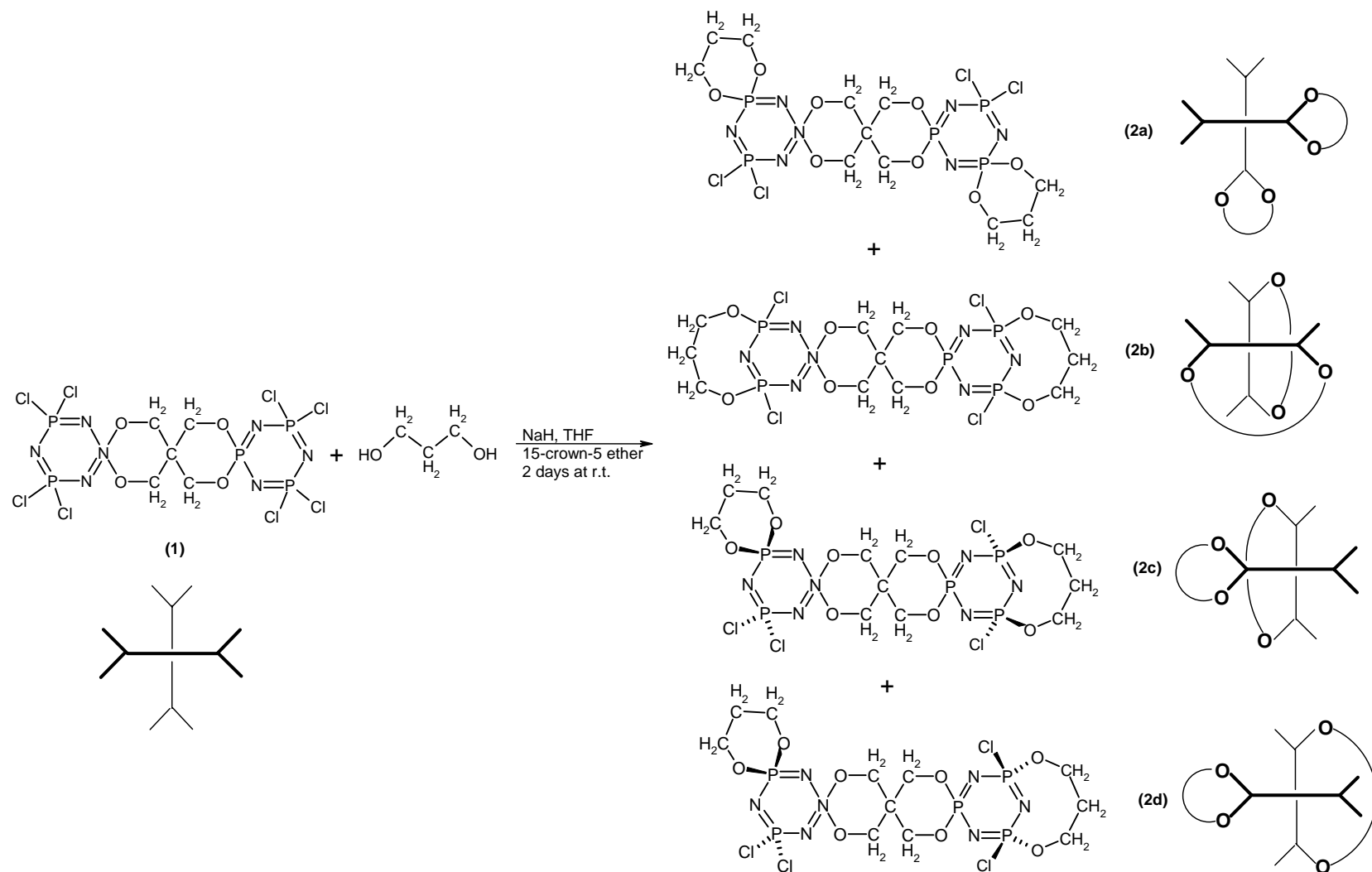
<sup>d</sup> No separation of signals observed up to a mole ratio of CSA:(**2**) of 50:1

<sup>e</sup> No separation of signals observed up to a mole ratio of CSA:(**2**) of 40:1

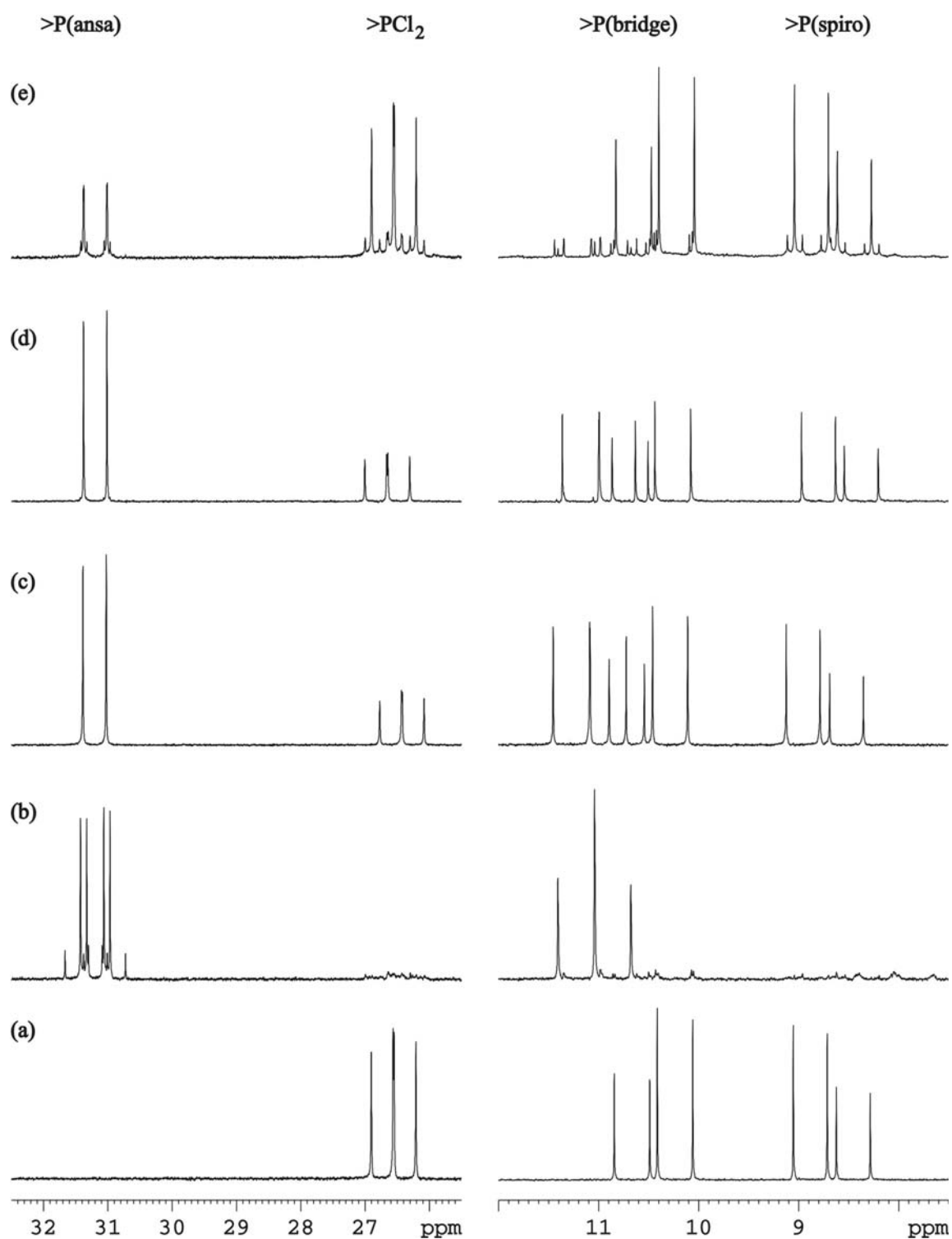
**Table 2** X-ray data for compounds (**2c**) and (**2d**)<sup>a</sup>

	( <b>2c</b> )	( <b>2d</b> )
Empirical formula	$\text{C}_{11}\text{H}_{20}\text{Cl}_4\text{N}_6\text{O}_8\text{P}_6$	$\text{C}_{11}\text{H}_{20}\text{Cl}_4\text{N}_6\text{O}_8\text{P}_6$
Formula weight	691.95	691.95
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	12.1255(3)	14.7211(3)
<i>b</i> (Å)	10.7597(3)	11.9459(3)
<i>c</i> (Å)	23.7161(5)	14.9661(4)
$\beta$ (°)	90	105.089(2)
Volume (Å <sup>3</sup> )	3094.16(13)	2541.15(11)
<i>Z</i>	4	4
Density (calc) (Mg/m <sup>3</sup> )	1.485	1.809
Absorption coefficient (mm <sup>-1</sup> )	0.735	0.895
<i>F</i> (000)	1400	1400
Crystal size (mm)	0.45 × 0.40 × 0.40	0.12 × 0.10 × 0.01
$\theta_{\text{max}}$ (°)	27.49	27.46
Reflections collected	25948	34251
Independent reflections	3716	5808
Final <i>R</i> indices $F^2 > 2\sigma F^2$	<i>RI</i> = 0.1070 <i>wRI</i> = 0.2769	<i>RI</i> = 0.0362 <i>wRI</i> = 0.0754
$\Delta\rho_{\text{max/min}}$ (eÅ <sup>-3</sup> )	1.236/−1.017	0.369/−0.427

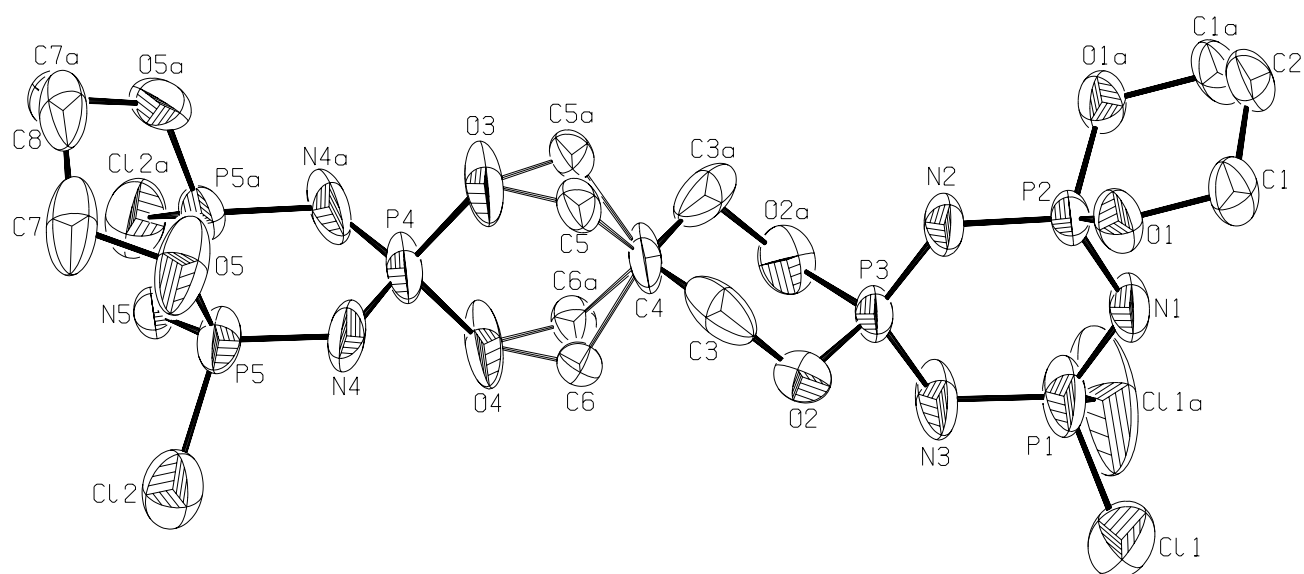
<sup>a</sup> Full details of data collection and structure determination have been deposited with the Cambridge Data Centre, deposition numbers CCDC 245906 and CCDC 245907.



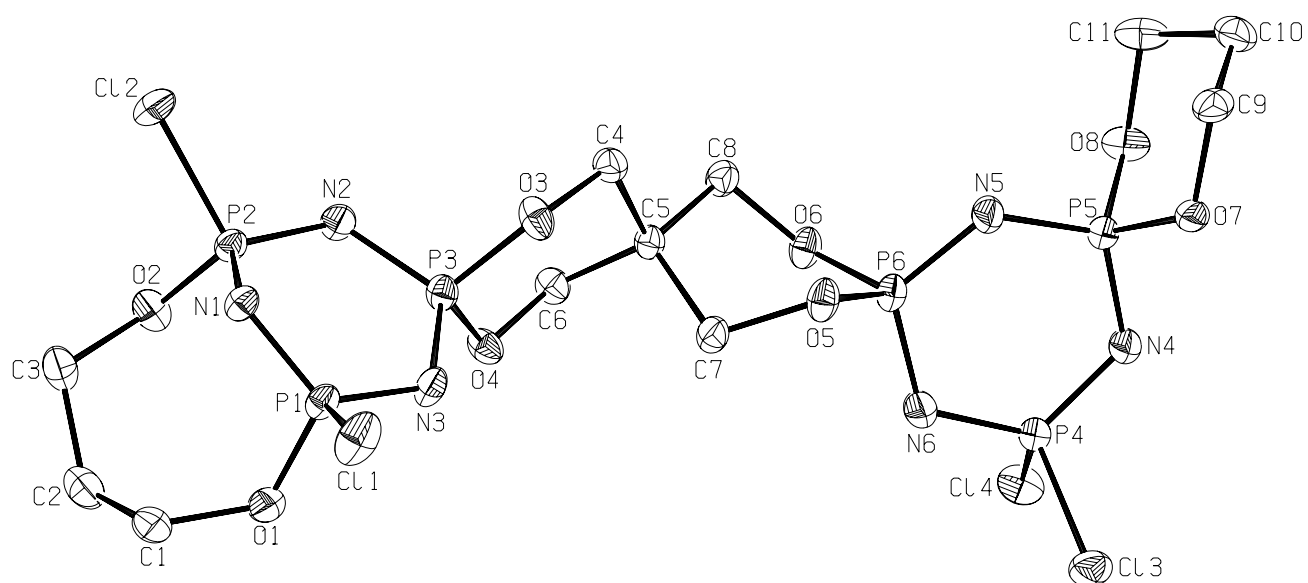
**Fig. 1** Structures of spiroane-bridged unsubstituted, (1), and disubstituted cyclotriphosphazene derivatives; di-monoansa (2a), di-monoansa (2b), and two monospiro-monoansa derivatives (2c, syn) and (2d, anti). A diagrammatic representation is also shown for compounds (1, 2a–2d). For clarity the inner organophosphate rings have been omitted and the outer cyclophosphazene rings, which are orthogonal to each other, are shown in the same projection with the ring to the front in bold type.



**Fig. 2**  $^{31}\text{P}$  NMR spectra of the reaction mixture and the isolated four isomers of 1,3-propanedioxy derivatives of pentaerythritol-bridged cyclotriphosphazenes. (a) **2a**, spiro-spiro, (b) **2b**, ansa-ansa, (c) **2c**, syn spiro-ansa, (d) **2d**, anti spiro-ansa, (e) reaction mixture



2c (syn)



2d (anti)

**Fig. 3** X-ray crystal structures of the two monospiro-monoansa derivatives (**2c**) and (**2d**). The plane of symmetry in each molecule can be clearly seen in the diagrammatic representation of the structures in Fig.1.

## Graphical Abstract

